

Field Electron Emission from Pyrograf III PR-1 Carbon Nanotube Fibers Embedded in Glass

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Abstract: This study investigates the field electron emission properties of Pyrograf-III carbon nanotube fibers (CNTFs). Field emitters were manufactured by employing a drawing technique using a glass puller. A field electron microscope with a tip (cathode) to screen (anode) separation of approximately 10 mm was used to characterize the emitters. The current-voltage (I - V) characteristics of the CNTFs showed a shallow increase in the emitted current with increasing applied voltage, until a threshold voltage (V_{TH}) is reached, after which a “switch-on” phenomenon occurs. The I - V characteristics are then linear. Fowler-Nordheim plots and field electron emission patterns are also discussed and it is shown that it is possible to get a single bright emission spot.

Keywords: Field electron emission, Carbon nanotube fibers (CNTFs).

Introduction

Field electron emission (FE) involves electron emission from surfaces that is caused by high electric fields. It has been extensively studied since the late 1920s, after Fowler and Nordheim (FN) developed (in 1928) the first good model for electron emission from planar surfaces. Fowler and Nordheim assumed a single electron band, with the electron distribution in thermodynamic equilibrium at 0 K and an emitter with a flat planar surface of constant uniform local work function, with a uniform field outside it.

Carbon nanotubes (CNTs) have attracted many researchers, from a wide range of fields from academia to industry. This is not only because of their uniqueness when compared with conventional materials, but also because they are very promising FE materials, due to their properties, which include high aspect ratio, mechanical and chemical stability [2] and high

melting point as compared with conventional metal emitters. This enhanced performance has encouraged the development of many applications.

There are several types of CNT. Multi-walled carbon nanotubes (MWCNTs) were discovered in 1991 by Sumio Iijima. He found an extremely thin needle-like material when examining carbon materials using electron microscopy [3] and found the "needles" to be composed of multi-wall tubes nesting concentrically. Later, in 1993, a single-walled carbon nanotube was discovered [4]. Carbon nanotube fibers (CNTFs) are a newly designed composite material [5] based on carbon nanotubes, as shown in Fig. 1. CNTFs have radii that are much smaller than those of conventional continuous or milled carbon fibers (5-10) μm , but are significantly larger than those of carbon nanotubes (1-10) nm [5].

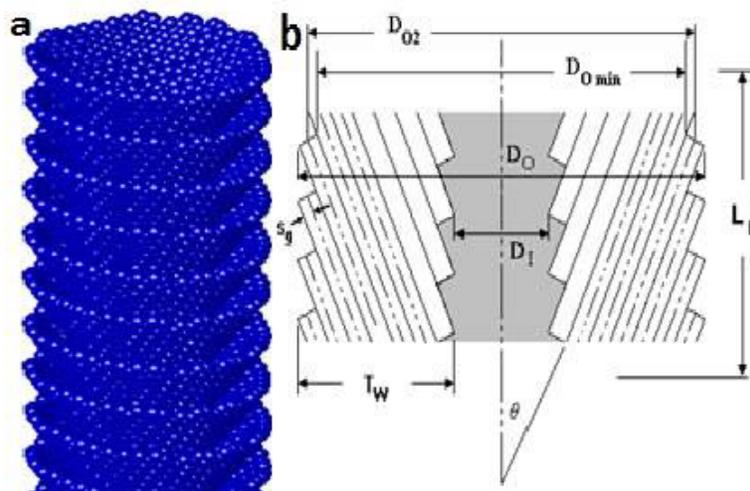


FIG. 1. (a) Artist's depiction of pyrograf II stacked-cup carbon nanotubes. (b) Cross-sectional view showing the internal structure of the pyrograf product stacked-up carbon nanotubes.

As a result of their tremendous properties, many potential applications have been proposed for CNTs and there is much interest in applications for life both now and in the future. Such applications may include electrochemical devices, hydrogen storage, sensors, high frequency electronics and more [6, 7].

In our work, the main aim behind choosing this design of emitter was to try to get emission images that consist of single bright spots. If this can be achieved, this type of electron source might be suitable as an electron microscope source.

According to the Fowler-Nordheim model (e.g., [8]), emission from planar or large-radius surfaces produces straight lines in a so-called Fowler-Nordheim (FN) plot [i.e., a plot of $\ln(I/V^2)$ vs. $1/V$ or alternatively $\log_{10}(I/V^2)$ vs. $1/V$]. However, almost all experimental FN plots for CNT field emitters deviate from straight lines. Possible reasons have been discussed elsewhere [8, 9].

Field electron emission (FE) occurs when the electric field strength is a few V/nm. In order to produce such high electric fields, the emitter is usually formed by a tiny tip, which has an apex radius ranging from several nanometers to sub-micrometers [10]. There are several ways to produce such a tip; we manufactured our tips by employing a drawing technique using a glass puller. To make sure that the CNTFs protrude, we break the apex of the glass tube. Fig. 2 shows a schematic diagram of the glass puller [11].

In this paper, we will discuss the current – voltage characteristics and FN plots extracted

from Pyrograf III PR-1 CNTFs. The average fiber diameter is (100-200) nm and the length is (30-100) μm .

Materials and Methods

As already indicated, our emitters were prepared by the technique of pulling heated glass capillary tubes into a fine point [12]. In this technique, two bearings are located accurately on plates supported by three stainless steel rods fixed rigidly to the frame of the control unit. This frame is strong enough to serve as a stable base for the instrument. A glass tube (outside diameter = 1mm, internal diameter = 0.1 mm) fits inside these bearings, between the upper and lower chucks, with a furnace loop located around it. The CNTFs were entered into the opposite ends of each glass tube with a wire plunger and the apex was broken deliberately, so that they would protrude at the end. The lower chuck spindle can slide vertically, in order to pull the glass tube under gravity [11].

A result of applying this technique is shown in Fig. 3.

The analyses were carried out using a standard field electron emission microscope [12]. The system had been evacuated to a pressure of 10^{-7} mbar after baking at around 140 °C overnight. The axial tip-screen separation is standardized at approximately 10 mm [11]. The current-voltage characteristics and related Fowler-Nordheim (FN) plots have been investigated for two samples.

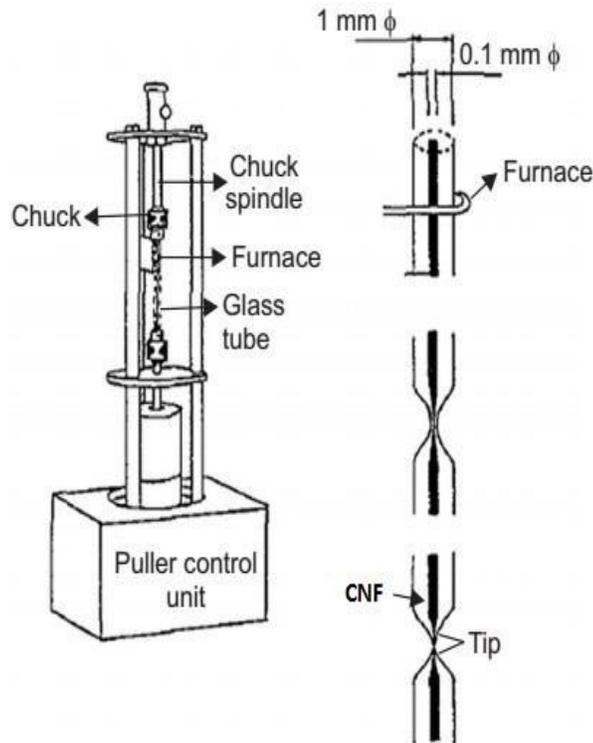


FIG. 2. A schematic diagram of the glass puller.

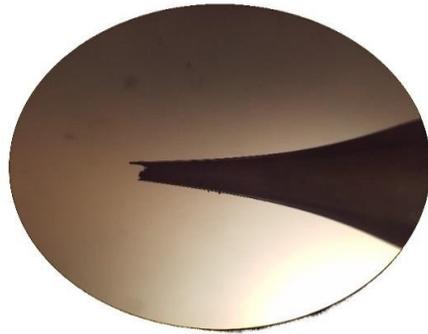


FIG. 3. Optical image of a glass capillary tube that contains CNTFs. Sample No. (CNTF-26) tip at X 50 magnification.

Results and Discussion

The behavior of the Pyrograf III PR-1 carbon nanotube fiber is shown in Fig. 4 as the I - V characteristics. Increasing the applied voltage very slowly caused an increase in the emission current until a certain value (V_{sw}) is reached, where electron emission is suddenly initiated by a “switch-on” process. This involves the switching-on of the emission current from zero to a value of a few tenths of μA . In sample CNTF-26, this switch-on occurs at $V_{sw} = 1000$ V, with an emission current of $4.8 \mu\text{A}$, as Fig. 4 shows. Fig. 5 shows the emission image at V_{sw} .

On further increasing the applied voltage, the emission current reaches $8.49 \mu\text{A}$ at $V = 1350$ V.

On decreasing the voltage, a constant-resistance regime was detected, down to a voltage $V_C = 320$ V, at which a regime change occurs (at emission current of $1.11 \mu\text{A}$). Beyond this, the current falls smoothly towards zero as the applied voltage is decreased to a threshold value $V_{TH} = 120$ V (this is the gate voltage threshold for measurable field emission current, defined as 5 pA). Fig. 6 shows this I - V behavior, the related FN plot at decreasing voltage and some emission images that show an electron image spot that is bigger and brighter at higher applied voltage.

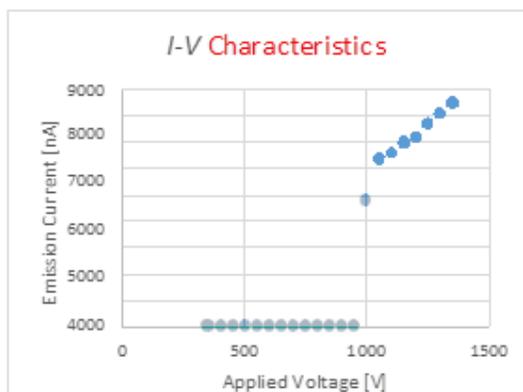


FIG. 4. Increasing voltage: the I-V characteristics for CNTF-26.

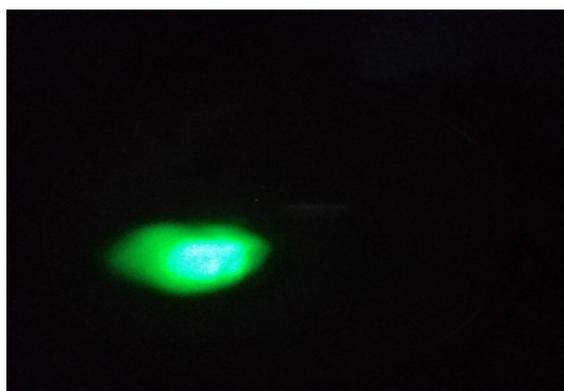


FIG. 5. Increasing voltage: field electron microscope image at $V_{sw} = 1000$ V, $I_{sw} = 4.8$ μ A.

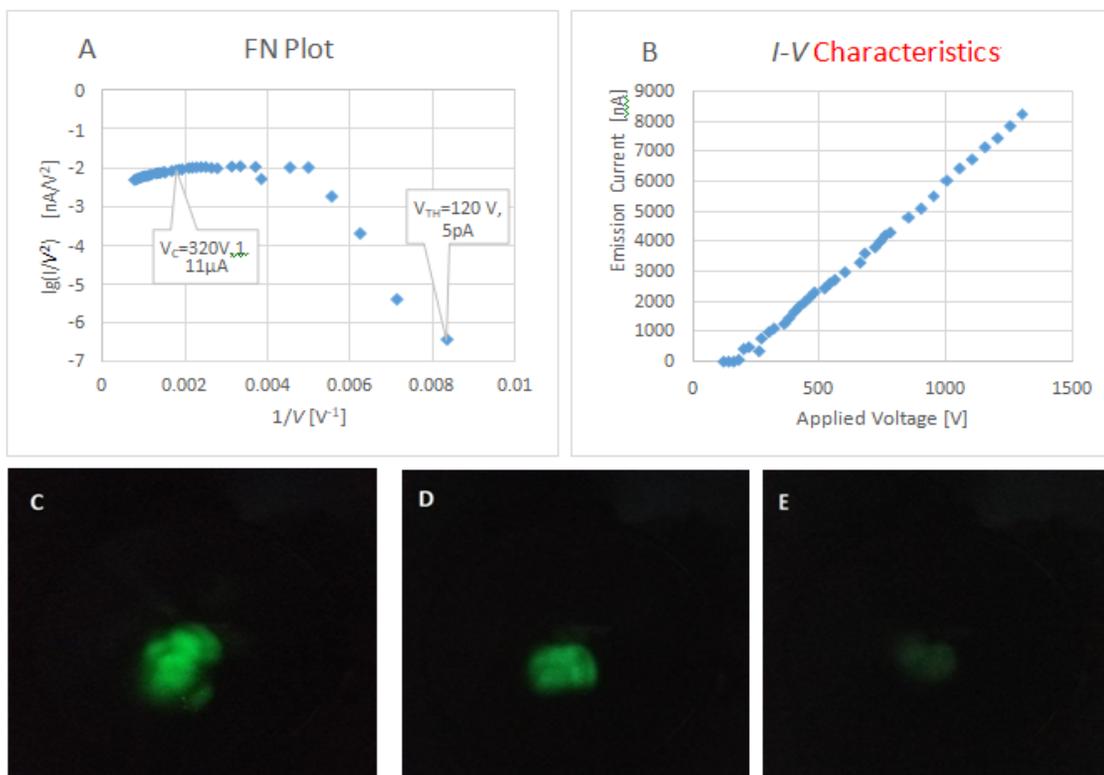


FIG. 6. Decreasing voltage: (A) FN Plot of tip CNTF-26 with slope (-1394.01) decade V. (B) I-V characteristics (C) Emission image at $V_{SAT} = 740$ V; 4 μ A (D) Emission image at $V = 600$ V; 2.98 μ A. (E) Emission image at $V = 320$ V; 1.11 μ A.

Studies were also carried out on a second tip (Pyrograf III PR-1 CNTF No. 25). The optical micrograph in Fig. 7A shows the shape of the end of the glass tube in which the tip is embedded. The voltage was cycled up and down two times and the I - V characteristics and FN plots have been studied for both cycles.

As the applied voltage is slowly increased, the emission current increases from $I=20$ pA to $I=12.3$ μ A. Figs. 7B and 7C show that for this emitter, the switch-on occurs at $V_{sw} = 750$ V, at an emission current of 3.6 μ A. The current then increases linearly, again indicating a constant-resistance regime. On reducing the applied voltage, the linear region extends down to $V=350$ V, at an emission current of 1.09 μ A.

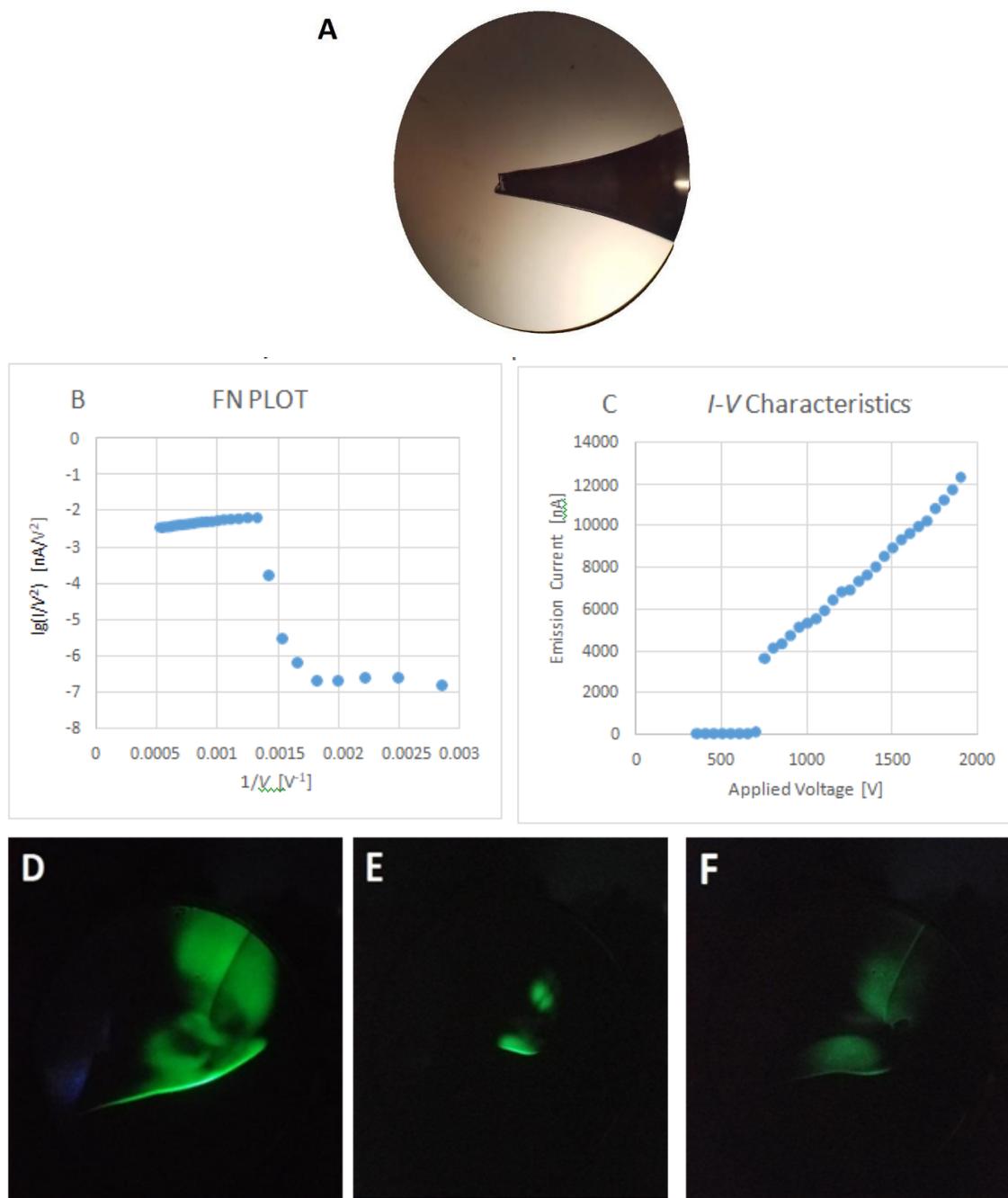


FIG. 7. (A) Optical image of a glass capillary tube that contains CNTFs. Sample No. (CNTF-25) tip at X 50 magnification. (B) FN plot.(C) I-V characteristics. (D) Emission image at $V_{sw} = 750$ V; 3.6 μ A. (E) Emission image before switch-on at $V=700$ V; 80 nA. (F) Emission image at $V_{SAT} = 350$ V; 1.09 μ A.

In both cases, the FN plot "saturates" even though the current-voltage relationship is linear. This shows clearly that FN-plot saturation can be a mathematical effect that occurs even though the emission current does not physically saturate.

We then repeated the experiment for the same tip (CNTF Pyrograf III PR-1 No. 25) under the same conditions. Fig. 8 and the following figures show the cycle of increasing and decreasing the applied voltage. Figs. 8A and 8B show that the emission current increases from 20

pA to 8.34 μA , without showing "switch-on" phenomenon as voltage increases from 200 V to 1450 V. When the voltage is decreased, the emission current decreases linearly from 8 μA to 8 pA, beyond which the current falls smoothly towards zero as the applied voltage is decreased to a threshold value $V_{\text{TH}} = 150$ V (where the emission current is 8 pA), as Fig. 9 shows.

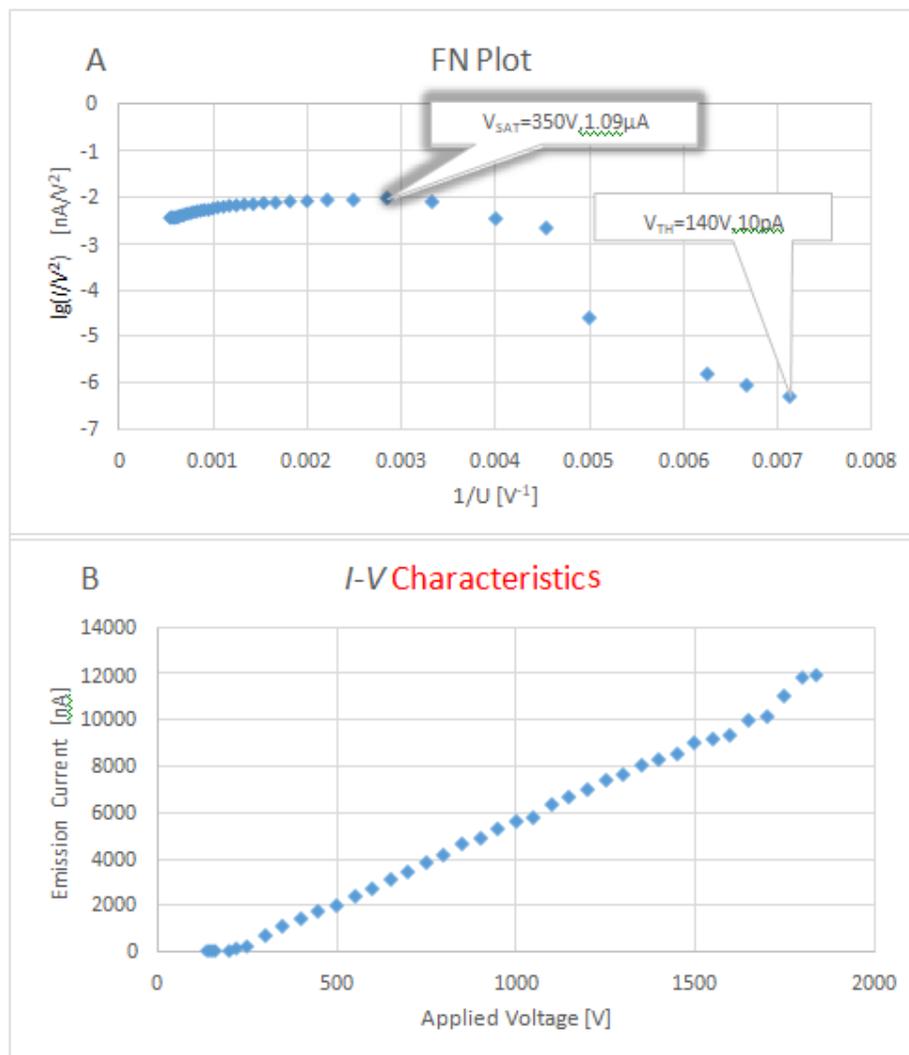


FIG. 8. CNTF-26 decreasing voltage. (A) FN plot with slope (-1296) decade V. (B) I-V characteristics.

Fig. 11 shows a collection of emission images during the second cycle of voltage. In contrast to the first cycle, the emitter produces a single bright spot and we notice that increasing the applied voltage causes the spot to spread.

As indicated above, the current-voltage characteristics are linear, suggesting that there is a large resistance somewhere in the circuit. This causes the FN plots to be non-linear and may also lead to voltage drops in the circuit that would cause shifts in the total electron energy

distribution. If these shifts happen, they would probably make this form of emitter unsuitable as an electron microscope source. There may also be other reasons behind the non-linearity in the

FN plots, such as adsorption effects, emission-current dependence in the field enhancement factor or local conversion length and conceivably space-charge effects.

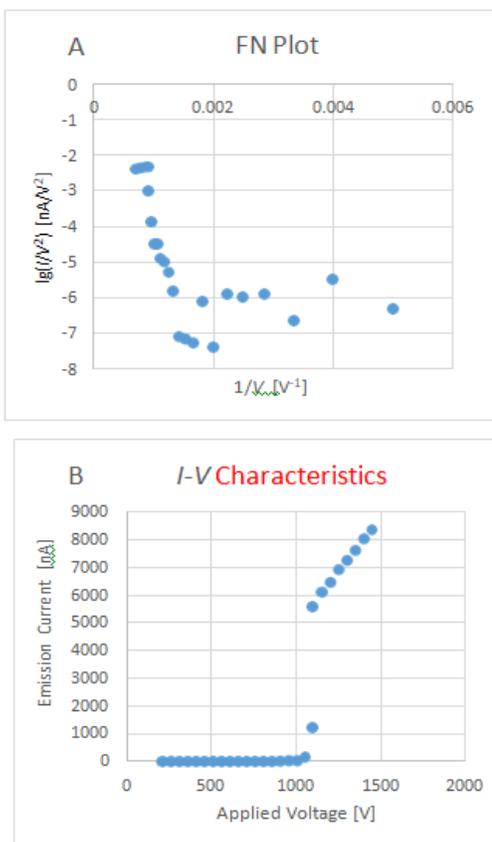


FIG. 9. Increasing voltage: (A) FN Plot for tip CNTF-25 (B) I-V characteristics range (200-1450)V with emission current range (20 pA - 8.34 μ A).

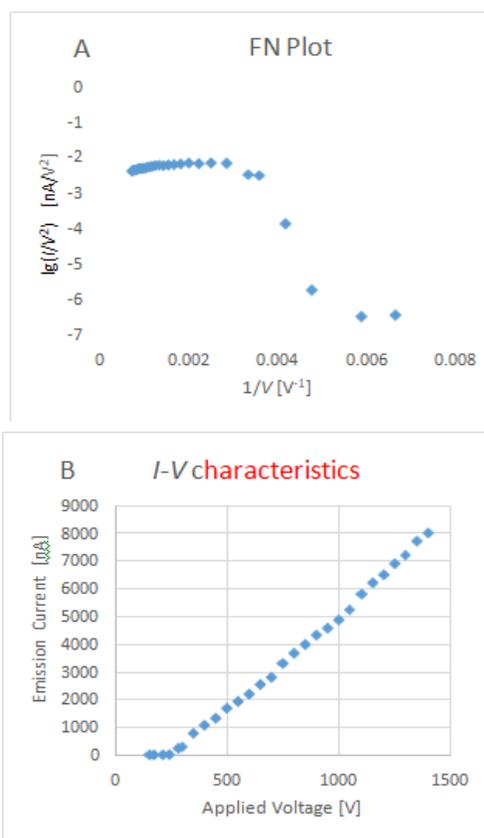


FIG. 10. Decreasing voltage: (A) FN plot for tip CNTF-25. (B) I-V characteristics range (150-1400) V, with emission current range (8 pA - 8 μ A).

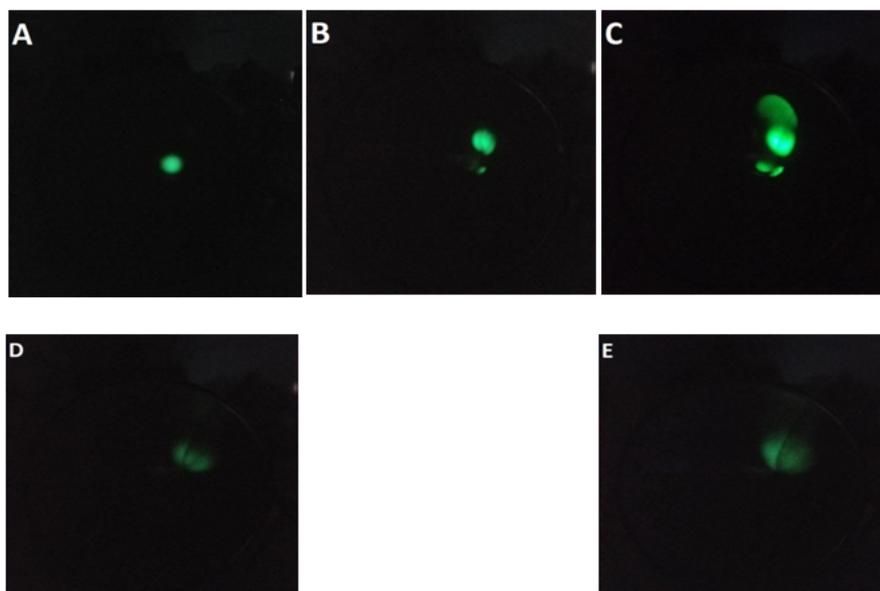


FIG. 11. By increasing voltage, emission images at voltage values: (A) 850 V, $I=7.2$ nA. (B) 950 V, $I=20.81$ nA. (C) 1050 V, $I=0.157$ μ A. By decreasing voltage (D) $V=280$ V, $I=0.24$ μ A. (E) $V=300$ V, $I=0.29$ μ A.

We also note that, in some emission images in Fig. 7, there are irregularities and a bright streak at the edge of the image. The cause of this could be the irregular shape of the CNTFs or possibly charging of the end of the glass tube (Forbes, private communication, 2017).

The importance of CNTs and related materials has led scientists to make extensive investigations to understand their FE behavior. For CNTFs, detailed studies have been conducted by Cahay and collaborators [13], who looked at many of the factors that influence FE, including the density of active field emitters (assuming that the CNTFs splay apart at the ends into individual CNTs), the emission mechanism, the emission geometry, the fiber condition, current-voltage loop behavior and outgassing issues. Fig. (12) compares their I - V characteristics with ours.

Fig. (12A) shows Cahay's characteristics [13] for CNTFs at different separations (d_{gap}) between

anode and cathode (2, 1.75, 1.50, 1.25 mm), where E_{AG} is the “apparent gap field” defined by V/d_{gap} and V is the measured voltage between anode and the grounded cathode. These characteristics should be compared with our characteristics as shown in Figs. 7C and 9A. The two sets of characteristics are not quite the same, because the characteristics as found by Cahay et al. [13] exhibit a departure from linearity at high fields and voltages. Also, in our experiments, the distance between cathode and anode was 10 mm and the highest emission current ranged between 8 and 12.2 μA ; in Cahay's experiments (at significantly smaller gaps), the highest emission current ranged between 0.6 and 2.2 mA. There are various possible reasons for the differences between our results and Cahay's results, including the likelihood that Cahay's emitters have a different physical structure from ours. We hope to explore these matters further in future studies.

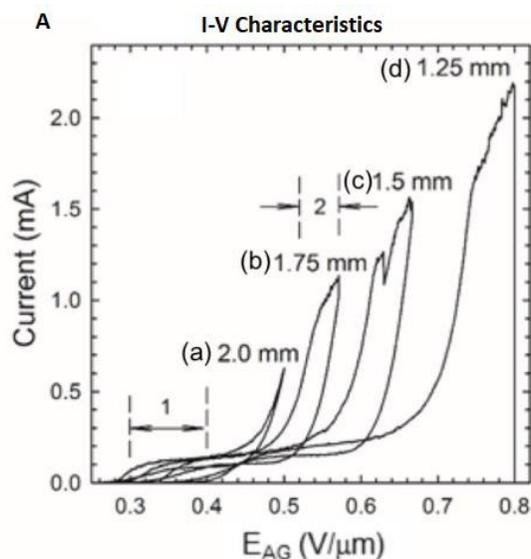


FIG. 12. I-V characteristics for CNTFs after Cahay [13], for different distances between anode and cathode.

Conclusions

Pyrograf III PR-1 carbon nanotube fiber emitters have been prepared by employing a drawing technique using a glass puller and their I - V characteristics, FN plots and emission images have been studied. These sources seem capable of producing a single bright field electron emission spot. This may be of potential use in some electron-beam applications, but these emitters will probably be unsuitable as electron microscope sources, for the following reasons. We have been employing a locally

smooth emitter tip, embedded in a glass tube. The single emission spot occurs at low applied voltage, where the number of separate emission sites is lowest. Because of the nonmetallic nature of the tip, field penetration, fluctuation of the applied potential, shifts in the position of the emitting levels, and particularly if the current flow through the emitter leads to significant voltage loss (in accordance with Ohm's law), there may be current-dependent shifts in the emitter energy distribution. These shifts would make the source unsuitable as a source for an electron microscope (or for any other electron

beam instrument where sharp focusing is required).

The most interesting feature of our results is perhaps the fact that our current-voltage characteristics are linear; hence the measured current-voltage characteristics do not obey any Fowler-Nordheim-like equation and the related FN plots have a curious characteristic non-linear shape. Experimental FE situations that generate linear I - V characteristics are relatively unusual.

We have also established that our CNTFs appear to have slightly different behavior from those of Cahay et al. [13]; the reasons for this difference remain to be explored.

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